

What is claimed is:

1. An electrolytic copper plating solution containing a compound having the structure represented by the formula of -X-S-Y-

wherein each of X and Y independently represents an atom selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, and a thiol-reactive compound.

2. The electrolytic copper plating solution according to claim 1, wherein the compound having the structure represented by the formula of -X-S-Y-

wherein each of X and Y independently represents an atom selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, is selected from the group consisting of:

- (1) $M-SO_3-(CH_2)_a-S-(CH_2)_b-SO_3-M$;
- (2) $M-SO_3-(CH_2)_a-O-CH_2-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (3) $M-SO_3-(CH_2)_a-S-S-(CH_2)_b-SO_3-M$;
- (4) $M-SO_3-(CH_2)_a-O-CH_2-S-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (5) $M-SO_3-(CH_2)_a-S-C(=S)-S-(CH_2)_b-SO_3-M$;
- (6) $M-SO_3-(CH_2)_a-O-CH_2-S-C(=S)-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (7) $A-S-(CH_2)_a-SO_3-M$; and
- (8) $A-S-CH_2-O-(CH_2)_a-SO_3-M$

wherein each of a and b represents an integer in the range of 3 to 8; M represents a hydrogen or alkali metal element; A represents one selected from the group of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an aryl group, a acyclic or cyclic amine compound consisting of 1 to 6 nitrogen atoms, 1 to 20 carbon atoms, and a plurality of hydrogen atoms, and a heterocyclic compound consisting of 1 to 2 sulfur atoms, 1 to 6 nitrogen atoms, 1 to 20 carbon atoms, and a plurality of hydrogen atoms.

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3. The electrolytic copper plating solution according to claim 1,
wherein the electrolytic copper plating solution contains 0.1 to 100
mg/L of the compound having the structure represented by the
5 formula of -X-S-Y-.

4. The electrolytic copper plating solution according to any one of claims
1 to 3, wherein the thiol-reactive compound is at least one selected from
the group consisting of carboxylic acid, peroxy acid, aldehyde and ketone
10 of aliphatic compounds, alicyclic compounds, aromatic compounds or
heterocyclic compounds and hydrogen peroxide.

5. The electrolytic copper plating solution according to claim 4, wherein
the thiol-reactive compound is present in the electrolytic copper plating
15 solution in an amount from 1.0×10^{-4} to 1.0×10^{-1} mol/L.

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6. A process for electrolytic copper plating layer to a substrate using the
electrolytic copper plating solution according to any one of claims 1 to 5.

7. The method for electrolytic copper plating of claim 6, wherein the
substrate is a printed wiring board or a wafer.

8. The process for electrolytic copper plating of claim 7, wherein the
substrate has a through hole or a via hole.

9. A composite material, which is prepared by the process for
electrolytic copper plating according to any one of claims 6 to 8.

10. A method for controlling an electrolytic copper plating solution
containing a the compound having the structure represented by the
30 formula of -X-S-Y-

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wherein each of X and Y independently represents an atom

selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, and a thiol-reactive compound, comprising adding a thiol-reactive compound and maintain the concentration of the compound having -X-S- structure equal or less than 1.0 micro mol/L.

11. The method for controlling an electrolytic copper plating solution according to claim 10, wherein the compound having the structure represented by the formula of -X-S-Y- wherein each of X and Y independently represents an atom selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, is selected from the group consisting of:

- (1) $M-SO_3-(CH_2)_a-S-(CH_2)_b-SO_3-M$;
- (2) $M-SO_3-(CH_2)_a-O-CH_2-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (3) $M-SO_3-(CH_2)_a-S-S-(CH_2)_b-SO_3-M$;
- (4) $M-SO_3-(CH_2)_a-O-CH_2-S-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (5) $M-SO_3-(CH_2)_a-S-C(=S)-S-(CH_2)_b-SO_3-M$;
- (6) $M-SO_3-(CH_2)_a-O-CH_2-S-C(=S)-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (7) $A-S-(CH_2)_a-SO_3-M$; and
- (8) $A-S-CH_2-O-(CH_2)_a-SO_3-M$

wherein each of a and b represents an integer in the range of 3 to 8; M represents a hydrogen or alkali metal element; A represents one selected from the group of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an aryl group, a acyclic or cyclic amine compound consisting of 1 to 6 nitrogen atoms, 1 to 20 carbon atoms, and a plurality of hydrogen atoms, and a heterocyclic compound consisting of 1 to 2 sulfur atoms, 1 to 6 nitrogen atoms, 1 to 20 carbon atoms, and a plurality of hydrogen atoms.

12. The method for controlling an electrolytic copper plating solution according to claim 10 or 11, wherein the thiol-reactive compound is at least one selected from the group consisting of carboxylic acid, peroxy acid, aldehyde and ketone of aliphatic compounds, alicyclic compounds, aromatic compounds or heterocyclic compounds and hydrogen peroxide.

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